



Original Article

The effect of quartz on the flotation of pyrite depressed by serpentine[☆]



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ABSTRACT

The effect of quartz particles on the flotation of pyrite depressed by serpentine has been investigated through flotation tests, adsorption tests, zeta potential measurements and DLVO calculation. The results show that the presence of hydrophilic serpentine slimes on pyrite surface reduces collector adsorption and results in lower recovery of pyrite. The finer the serpentine slime is, the lower the pyrite recovery will be. Quartz particles do not interfere with pyrite flotation. However, the addition of quartz particles increases the adsorption of collector on pyrite surface and limits the detrimental effect of serpentine on pyrite flotation. The fine-grained quartz is more effective. Zeta potential measurements and DLVO calculation illustrate that the zeta potential of quartz is more negative than that of pyrite and the attraction force between serpentine and quartz is stronger than force between serpentine and pyrite, thus some serpentine slimes were transferred from pyrite surface to quartz in the process of attrition.

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1. Introduction

Jinchuan concentrators process sulphide ores using froth flotation to produce a concentrate averaging 8.8% Ni, 4.8% Cu, 15.26% S, 28.16% Fe and 6.8% MgO. This concentrate is then further upgraded at the Nickel Smelter by burning off excess sulphur and removing the iron and MgO as a slag phase to produce a nickel sulphide rich matter.

Serpentine is the main magnesium-rich phyllosilicate mineral in Jinchuan nickel sulphide ore. Due to its low hardness, serpentine is easily slimed. The fines or slimes possess an opposite charge to the coarse sulphide particles. This creates an electrostatic attraction force which results in the slimes forming a coating over the surface of the coarse particles [1–3]. A coating of hydrophilic slime particles will decrease the flotation recovery of sulphide particle. In order to limit the effect of serpentine slime on sulphide flotation,

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sodium hexametaphosphate, sodium silicate, carboxymethyl cellulose (CMC), and sodium carbonate are used to remove serpentine slime from sulfide surfaces [4-7]. However, high reagent dosages are needed for dispersing serpentine slime and they contribute to considerable economic pressures.

The pioneering work of Gaudin shows that the adsorption of colloidal species is selective and the selective adsorption of colloidal species is relative to mineral surface potential [8]. For example, zinc metal hydrolysis products adsorb selectively on sphalerite surface in preference to the surfaces of galena or chalcopyrite [9]. Thus the selective adsorption of slimes on one mineral surface can be used to limit the detrimental effect of slimes on the other mineral flotation. In this investigation, quartz was used to remove serpentine slimes from pyrite surface. "Possibly, one can limit the detrimental effect of serpentine on sulphide flotation by adding to flotation system quartz particles or particles of other mineral, that are negatively charged and hydrophilic.

2. Experimental

2.1. Samples and reagents

The serpentine (lizardite) used for all experiments was obtained from Donghai, Jiangsu Province, China. Mineralogical and X-ray powder diffraction data confirmed that the serpentine sample was of high purity with trace amounts of chlorite and amphibole. The sample was dry ground and screened. Serpentine minerals with size of $-150 + 74 \mu\text{m}$, $-74 + 37 \mu\text{m}$ and $-10 \mu\text{m}$ were used for the flotation tests.

The pure quartz sample was obtained from Changsha, Hunan Province, China. The sample was dry ground and screened. The $-74 + 37 \mu\text{m}$, $12 + 10 \mu\text{m}$ and $-10 \mu\text{m}$ were used for the flotation tests.

Pyrite was obtained from Yunfu, Guangdong Province, China. The result of chemical analysis showed that the composition included Fe 44.96% and S 52.98%. The samples were dry ground and screened. The $-150 + 37 \mu\text{m}$ fraction was used for the flotation tests and $-37 \mu\text{m}$ for adsorption studies. The pyrite sample was stored in a vacuum-desiccator after prepared and washed in ultrasonic bath for 3 min to remove potential oxidation film before each use.

PAX (Potassium Amyl Xanthate) and MIBC (Methyl Isobutyl Carbinol) were used as collector and frother respectively. Potassium nitrate was used to maintain the ionic strength and HCL (hydrochloric acid) and KOH (potassium hydroxide) were used as pH regulators. All the reagents used in this study were of analytical grade. Deionized double distilled water was used for all tests.

2.2. Experiments

2.2.1. Flotation tests

Single mineral flotation tests were carried out in a mechanical agitation flotation machine (XFG). The impeller speed was fixed at 1800 r/min. The mineral suspension was prepared by adding 2.0 g of pyrite to 40 ml of distilled water. When needed, serpentine and quartz were added at the beginning of the conditioning period. The pH of the mineral suspension was

adjusted to the desired value by adding KOH or HCL stock solutions. The general reagent addition scheme involved collector and then frother addition with each stage having a 3 min conditioning period with air prior to the next reagent addition. Flotation concentrates were then collected for a total of 4 min. The floated and unfloated particles were collected, filtered and dried. The flotation recovery was calculated based on solid weight distributions and Fe grade between the two products.

2.2.2. Zeta potential measurements

Zeta potential measurements on pyrite, quartz and serpentine were carried out using a Coulter Delsa440 SX zeta potential meter. The working principle of the apparatus is Doppler electrophoresis effect and the zeta potential value was given by the zeta potential meter directly. Potassium nitrate was used to maintain the ionic strength at 10^{-3} mol/l . 30 mg sample ($-3 \mu\text{m}$) were added to 50 ml solution and ultrasonicated for 3 min, magnetically stirred for 10 min and the pH adjusted using HCL or KOH. Pulp pH was recorded using a pH meter (LeiCi PHS-3). The zeta potential of samples was then measured using a zeta potential meter.

2.2.3. Adsorption studies

For the adsorption tests, 1 g of mineral powder was taken and made up to 100 ml after addition of desired concentration of PAX solution in 250 ml Erlenmeyer flasks. The suspension was mixed and placed on a rotator for 5 min. The sample was then centrifuged and the concentration of PAX left in solution was analyzed using the UV absorbance at 301 nm. It was assumed that the amount of PAX depleted from solution had adsorbed onto the particular mineral phase.

3. Results and discussion

3.1. The effect of particle size of quartz on pyrite flotation in the presence of serpentine

The effect of pH on the floatability of pyrite, serpentine and quartz is shown in Fig. 1. It is evident from the picture that the flotation recovery of serpentine and quartz is independent of pH. The recovery of serpentine is low (20%) over the entire pH range tested and quartz does not have natural floatability. Different from serpentine and quartz, the flotation recovery of pyrite is very high under acidic and neutral conditions. As the pH was increased, pyrite recovery decreased due to formation of hydrophilic iron oxy-hydroxy species on the surface and the unstability of dixanthogen at high pH values [10,11].

The effect of serpentine and quartz on the flotation of pyrite at pH 9 is shown in Fig. 2. It can be seen from the picture that serpentine particles interfere with flotation of pyrite and their effect is related to their size, the finer the serpentine slime is, the lower the pyrite recovery will be. With the addition of $-150 + 74 \mu\text{m}$ fraction serpentine, pyrite recovery did not change, while when 5 g/L $-10 \mu\text{m}$ fraction serpentine particles were added, the recovery of pyrite decreased from 82 to 18%. Different from serpentine, the $-10 \mu\text{m}$ fraction quartz does not have effect on pyrite flotation.

The effect of quartz on the flotation of pyrite depressed by serpentine at pH 9 is shown in Fig. 3. Three kinds of particle

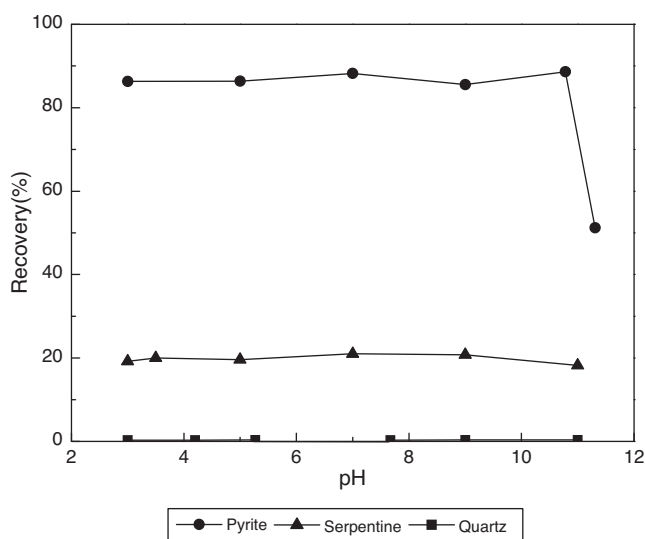


Fig. 1 – Effect of pH on the flotation recovery of quartz, serpentine and pyrite. ($c(\text{PAX}) = 1 \times 10^{-4} \text{ mol/l}$ and $c(\text{MIBC}) = 1 \times 10^{-4} \text{ mol/l}$).

size of quartz are used. It is interesting to note that the addition of quartz could restore the recovery of pyrite which had been depressed by serpentine. The recovery of pyrite increased with the increasing of quartz concentration and the finer the quartz particle size is, the higher the pyrite recovery is.

Fig. 4 shows the results of adsorption of PAX on pyrite. The presences of serpentine slimes decrease the adsorption density of PAX on pyrite surface, especially in alkaline pH range. This may be the main reason of serpentine interference with pyrite flotation. With the addition of quartz, the adsorption density of PAX on pyrite surface increased, illustrating that

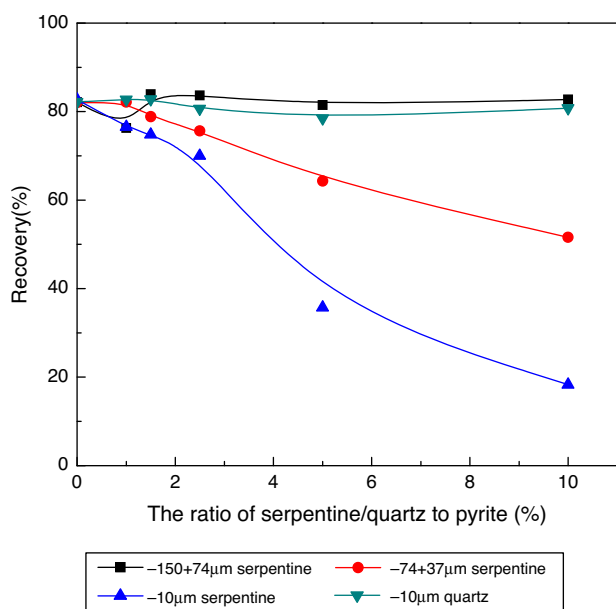


Fig. 2 – Effect of serpentine and quartz on the flotation recovery of pyrite. ($[\text{Pyrite}] = 50 \text{ g/L}$; $\text{pH} = 9.0$; $c(\text{PAX}) = 1 \times 10^{-4} \text{ mol/l}$ and $c(\text{MIBC}) = 1 \times 10^{-4} \text{ mol/l}$).

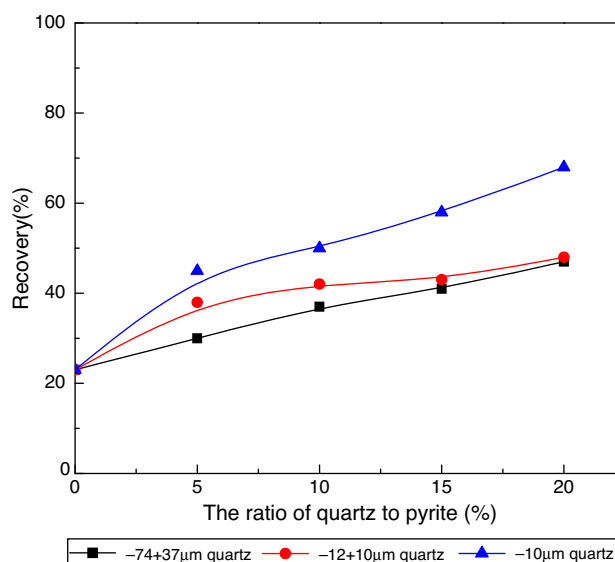


Fig. 3 – Recovery of pyrite as a function quartz concentration in the presence of serpentine ($[\text{Pyrite}] = 50 \text{ g/L}$; $[\text{Serpentine}] = 5 \text{ g/L}$; $\text{pH} = 9.0$, $c(\text{PAX}) = 1 \times 10^{-4} \text{ mol/l}$ and $c(\text{MIBC}) = 1 \times 10^{-4} \text{ mol/l}$).

quartz diminishes the effect of serpentine in decreasing collector adsorption on pyrite.

3.2. The mechanism of quartz limit the detrimental effect of serpentine on pyrite flotation

The use of quartz to improve the flotation of sulphide minerals is well known. However, there are different interpretations about the reason. Chander found that the flotation recovery of chalcopyrite increased with the increase of the proportion of quartz particles contained in a chalcopyrite quartz mixture. He thought that the removal of oxidation products from

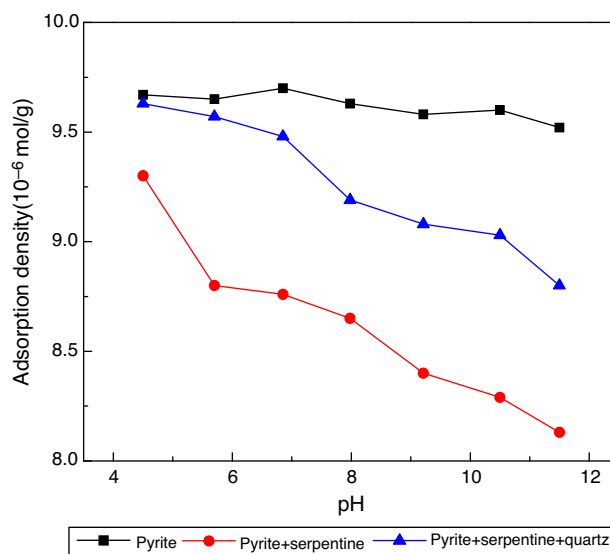


Fig. 4 – Adsorption of PAX onto pyrite. ($[\text{Pyrite}] = 10 \text{ g/L}$; $[\text{Serpentine}] = 0.5 \text{ g/L}$; $[\text{Quartz}] = 2 \text{ g/L}$; $\text{pH} = 9.0$, $c(\text{PAX}) = 10 \times 10^{-5} \text{ mol/l}$).

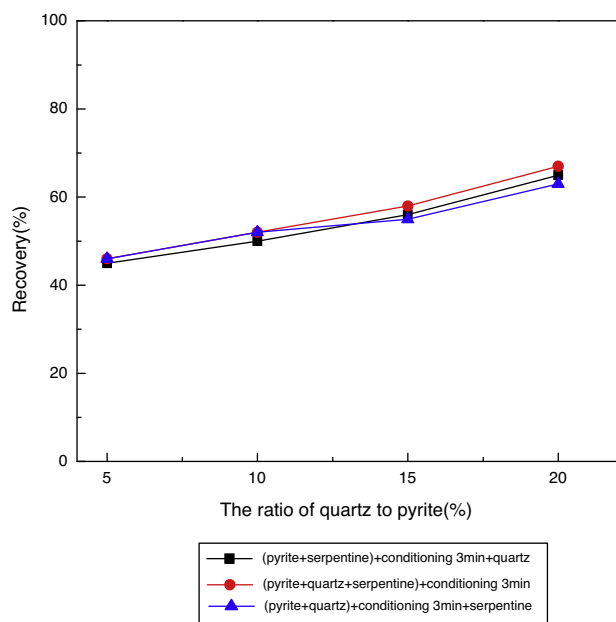


Fig. 5 – The effect of minerals addition order on pyrite flotation (pH = 9.0, $c(\text{PAX}) = 1 \times 10^{-4}$ mol/l and $c(\text{MIBC}) = 1 \times 10^{-4}$ mol/l).

a sulphide mineral surface by quartz seems to indicate that attritioning is the mode of surface cleaning by quartz [12]. Clarke found that sphalerite recovery increased up to 50% in the presence of quartz. He has attributed this behavior to the preferential adsorption or precipitation of metal hydroxides on the quartz surface rather than on the sulphide surface [9].

What is the main reason for the removal of serpentine slimes from pyrite surface? To ascertain this, the effect of minerals addition order on pyrite flotation is studied and the result is shown in Fig. 5. The result shows that the recovery of pyrite has no difference when quartz is added together with pyrite and conditioned 3 min before the addition of serpentine. This result illustrates that the adsorption of serpentine is not selective and the remove of serpentine slime from pyrite to quartz is the main reason for the increase of pyrite recovery.

The effect of conditioning time on pyrite flotation in the presence of serpentine and quartz is studied and the result is shown in Fig. 6. The result shows that the recovery of pyrite does not change when quartz is added together with pyrite and conditioned 3 min before the addition of serpentine, which indicates that, attritioning is not the main reason for the removal of serpentine slimes from pyrite surface by quartz.

The formation of slime coatings is controlled by the interaction energies between the slime and mineral particles and involves the process of aggregation. Aggregation between sulphide mineral particles and serpentine slime species is generally controlled by double layer interactions as van der Waals forces existing between dissimilar particles are generally attractive forces [13,14].

As a direct surface chemistry investigation of the different minerals, individual electro-kinetic studies of pyrite, serpentine and quartz particles as a function of pH in 0.001 M KNO_3 were undertaken. The results in Fig. 7 show that serpentine

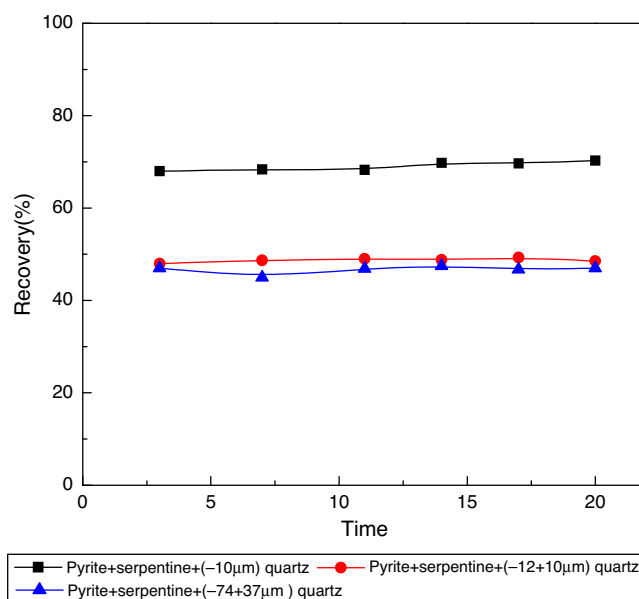


Fig. 6 – Recovery of pyrite as a function of conditioning time under different conditions. (pH = 9.0, $c(\text{PAX}) = 1 \times 10^{-4}$ mol/l and $c(\text{MIBC}) = 1 \times 10^{-4}$ mol/l).

has an iso-electric point (IEP) of pH 10.2. The zeta potential of serpentine is positive in the pH value range of 2–10.2. Fig. 7 also shows that the zeta potential of pyrite and quartz is negative at all pH values measured and the zeta potential of quartz is more negative than that of pyrite. At pH 9, it is likely that the positively charged fine serpentine particles will attach to the more negatively charged quartz particle surface rather than onto surface of pyrite particles through electrostatic attraction.

Particle interaction energies in aqueous solution are commonly described through application of DLVO theory, which allows quantitative prediction of the interaction energy. The interaction energy at constant surface potentials is often used

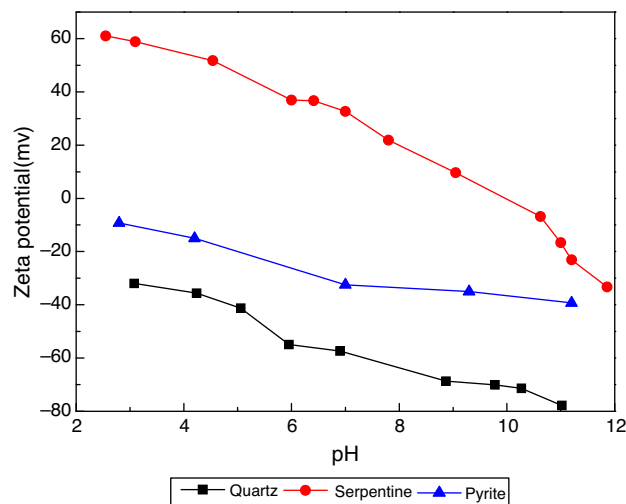


Fig. 7 – Zeta potential of minerals in 0.001 M KNO_3 as a function of pH.

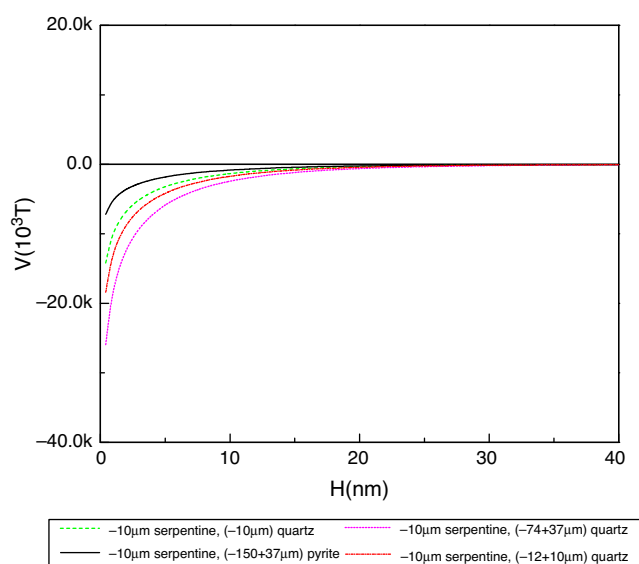


Fig. 8 – Interaction energy between a quartz/pyrite and serpentine particle.

and can be described by:

$$V_E = \frac{\pi \epsilon_0 \epsilon_r R_1 R_2}{(R_1 + R_2)} (\psi_1^2 + \psi_2^2) \times \left\{ \frac{2\psi_1 \psi_2}{(\psi_1^2 + \psi_2^2)} \times \ln \left[\frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)} \right] + \ln[1 - \exp(-2\kappa H)] \right\} \quad (1)$$

where the radius of serpentine particle is 3 μm, the radius of pyrite particle is 27 μm, the radius of quartz particle of different size fraction is 4 μm, 5.7 μm, 31 μm respectively; κ is the inverse thickness of the electric double-layer, $\kappa = 0.180 \text{ nm}^{-1}$; ϵ_0 , ϵ_r represents the vacuum dielectric constant and the relative dielectric constant of the continuous phase, and H represents the distance between particles; ψ_1 and ψ_2 are the surface potentials, when contact time between the particles is short, the assumption of constant surface charge is appropriate [15].

The van der Waals interaction energy is

$$V_W = -\frac{A}{6H} \frac{R_1 R_2}{R_1 + R_2} \quad (2)$$

The Hamaker constants for both serpentine/pyrite/water and serpentine/quartz/water are not available in literature. For pyrite, Chen lists a value of the Hamaker constant acting through vacuum as $A_{11} = 12.9 \times 10^{-20} \text{ J}$ [16]. As for serpentine and quartz, which is a magnesium silicate mineral, an approximation using the Hamaker constant for mica in vacuum could be used $A_{22} = 9.7 \times 10^{-20} \text{ J}$ [4]. The Hamaker constant (A_{123}) for two different materials (1 and 3) interacting through media (3) is

$$A_{123} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$

The zeta potential values for the serpentine, quartz and pyrite surface can be obtained from the electro-kinetic results in Fig. 7. The zeta potential values of serpentine, pyrite and

quartz at pH 9 are 9.6 mV, -32 mV and -70 mV respectively. The total interaction energy E was calculated by replacing the relative data into Eqs. (1) and (2), and the result is shown in Fig. 8. The total interaction energy between serpentine and pyrite is negative, as shown in Fig. 8. They attract each other and easily form aggregates. The total interaction energy between serpentine and quartz of the samples is more negative than that between serpentine and pyrite, which indicates that serpentine particles possibly would attach to the more negatively charged quartz particles. However, the -74 + 37 μm fraction quartz has the largest total interaction energy, what can be seen in Fig. 8, which is inconsistent with the flotation result presented in Fig. 3. One could explain this result by the largest surface area of the finest quartz particles and being able to remove more serpentine slime from pyrite surface.

4. Conclusions

- (1) The presence of hydrophilic serpentine slimes on pyrite surface reduces collector adsorption and results in lower recoveries of pyrite. The finer the serpentine slimes is, the lower the pyrite recovery will be.
- (2) Quartz particles do not interfere with the flotation of pyrite and can be used to limit the detrimental effect of serpentine on pyrite flotation; if so the fine-grained quartz is more effective.
- (3) The zeta potential value of quartz is more negative than that of pyrite and the attraction force between serpentine and quartz is stronger than that between serpentine and pyrite, thus some serpentine slime was removed from pyrite surface and transferred to quartz in the process of flotation.

Conflicts of interest

The authors declare no conflicts of interest.

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